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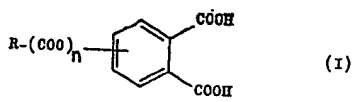
(54) PHTHALIC ACID DERIVATIVES

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4., England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to phthalic acid derivatives, which are suitable for use in detergent compositions adapted for fabric washing.

Detergent compositions commonly incorporate synthetic detergent active compounds together with detergency builders. Conventional detergency builders are commonly inorganic materials, particularly condensed phosphates, for example sodium tripolyphosphate. It has, however, been suggested that the use of phosphate detergency builders can contribute to eutrophication problems. Alternative organic detergency builders which have been proposed, for example sodium nitrilotriacetate (NTA) and synthetic polyelectrolyte materials, tend to be more expensive or less efficient than the phosphate detergency builders, or otherwise unsatisfactory for one reason or another. For example NTA contains nitrogen which is alleged also to be a contributory factor in eutrophication and the synthetic polyelectrolyte builders proposed tend to be hygroscopic and largely non-biodegradable.

The present invention provides phthalic acid derivatives having the general formula:



(I)

wherein R is an alkyl or alkenyl group containing from 10 to 20 carbon atoms, and n is 0 or 1, a hydroxyl group may be present in the benzene ring or in the alkyl group R, or an alkali metal, ammonium or substituted ammonium salt or the anhydride thereof.

The salts of these aromatic dicarboxylic acids act as detergency builders, generally by their forming insoluble salts with the calcium and magnesium ions present in hard water. Additionally, the aromatic dicarboxylic acid detergency builders can have useful fabric softening properties in the wash.

The novel compounds of the invention can be prepared by conventional organic chemistry techniques. Specifically, for example, the alkyl phthalic acids may be made by oxidation of alkyl o-xylenes, for example with oxygen in the presence of catalsyts such as cobaltous acetate or bromides such as manganese bromide: and the alkyl o-xylenes can be prepared by Friedel-Crafts addition of an alkyl group to o-xylene. For safety, it should be mentioned that the oxidation reaction must be carefully controlled to prevent an explosion with the cobalt catalyst. In the case of carbalkoxy phthalic acids, where an alkyl chain is attached by an ester group to the benzene ring the compounds may be made by reaction of an acyl chloride with a hydroxyphthalic acid.

The detergent compositions normally include in addition to the aromatic dicarboxylic acid detergency builders, one or more anionic, nonionic, amphoteric or zwitterionic detergent active compounds. Full details of suitable detergent compounds are found in the complete specification of the Patent Application No. 6682/72 (Serial No. 1425342).

The amount of the water-soluble or dispersible salt of the aromatic 1,2 - dicarboxylic acids used as detergency builders in the compositions is normally within the range of about 15% to about 80%, preferably at least about 30% by weight, depending on the desired properties of the compositions. When the compositions are intended for use at lower concentrations, for example in the range from about 0.05% to about 0.2% w/v, as is often the case in automatic

domestic [redacted]ng machines, such as commonly used in North America, it is preferable to have higher amounts of the water-soluble salts of the aromatic dicarboxylic acids present, for example at least about 35% and preferably 40—60% by weight. Although these amounts of the detergency builders have been expressed in terms of the amounts of salt used, it will be appreciated that the detergency builder may be in an acid or even anhydride form in the compositions in some cases, provided that the salt is formed on dissolution of the composition in water, and this necessitates including alkaline salts in the detergent compositions. It is however preferred to use the materials in a water-soluble salt form in the composition itself, the usual salts being the alkali metal salts, particularly the sodium, potassium or lithium salts, but ammonium or substituted ammonium salts for example the C_1—C_4 alkyl and alkanol ammonium salts can be used if desired.

The ratio of the detergent active compound to the detergency builders is generally in the range of from about 10:1 to 1:10, especially from about 3:1 to 1:5.

The aromatic dicarboxylic acid compounds of the present invention may be used as sole detergency builders, or in admixture with amounts of other detergency builders, as described in more detail in the parent specification, which also describes various optional detergent ingredients which may be added, and the physical forms of the compositions.

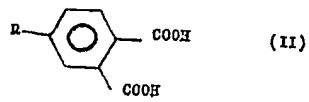
While the novel phthalic acid derivatives are of particular utility in compositions for fabric washing they can also be used for general cleaning purposes or if desired for personal washing.

Compositions according to the invention are illustrated by the Examples below, in all of which parts are by weight except where otherwise indicated.

Example 1

Prepene-tetramer (42.0 g, 0.25 m) was added dropwise over ½ hour to a vigorously-stirred mixture of o-xylene (103 g, 1.00 M) and 93% sulphuric acid (200 g about 2 M) at 0—3°, and the stirring was continued for a further 3 hours. The viscous, brown mass was poured onto ice (1 Kg), ether-extracted and the product was distilled to give unchanged xylene (92.1 g, 0.87 M; 87% recovery) and 1 - dodecyl - 3,4 - dimethylbenzene (35.2 g, 0.13 M; 50%).

A mixture of the alkyl xylene (12.5 g, 0.05 M), a solution of $MnBr_2 . 4H_2O$ (2.86 g, 0.01 M) in glacial acetic acid (500 ml), and oxygen (20 atm) was heated at 150° for 6 hours in a 1 litre stainless steel autoclave. Work-up of the product gave alkyl xylene (5.50 g, 0.02 M; 44% recovery) and 1 - dodecylbenzene - 3,4 - dicarboxylic acid (8.01 g, 0.024 M; 5[redacted] Spectroscopic and elemental analyses of the latter were consistent with the structure:



(II)

where R was a branched-chain dodecyl group.

About 10% of alkyl toluic acid was also present in the product.

The compound was examined as a detergency builder in the form of the sodium salt made in solution by the addition of sodium hydroxide, using a standard radioactive sebum test method in which the removal of the sebum (labelled with palmitic acid-1—C_{14}) from cotton cambric was examined at 45°C, pH=10, in a 10 minute wash. The detergent wash solutions contained 0.15% of the detergency builder and 0.05% of sodium dodecylbenzene sulphonate. The results for two water hardnesses are shown below including a comparative test result using sodium tripolyphosphate as the builder.

Detergency builder	Soil removal (%) 12.5°H	25°H
Sodium 1-dodecylbenzene-3,4-dicarboxylate	67	69
Sodium tripolyphosphate	82	66

The results indicate the compound to have some detergency building effect approaching that of sodium tripolyphosphate.

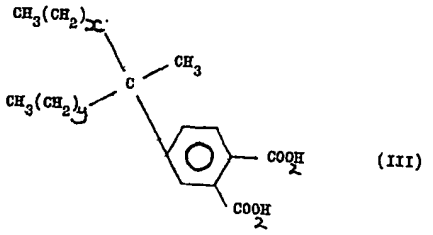
Further tests showed the alkyl phthalic acid compounds to have some fabric softening properties.

Example 2

A commercial C_{16} vinylidene olefin (containing 9% internal olefin) (56.0 g, 0.25 M) was added dropwise over 1 hour to a vigorously stirred mixture of 93% sulphuric acid (conc. H_2SO_4 49.0 g, 0.50 M, diluted to 93%) and o-xylene (106 g, 1.00 M) cooled to 0—5°C. The mixture was allowed to warm to room temperature and the stirring continued for 4 hours. Work-up in the usual way afforded unchanged xylene (50.1 g, 0.47 M; 47% recovery) and the product 1 - hexadecyl - 3,4 - dimethylbenzene (70.1 g, 0.24 M; 97%).

A 750 ml autoclave was charged with a mixture of the alkyl xylene (15.0 g, 0.05 M), a solution of $MnBr_2 . 4H_2O$ (2.86 g, 0.01 M) in glacial acetic acid (500 ml), and oxygen (20 atm). On heating, the pressure rose steadily to 25 atm until the temperature reached 145—150° when there was a rapid drop to 20 atm. After 3 hours at this temperature the pressure had

dropped slowly [redacted] atm. Isolated from the mixture were alkyl xylene (2.02 g, 0.01 M; 20% recovery) and a brown oil (13.5 g). The latter was found to comprise 82% of 1 - hexadecylbenzene - 3,4 - dicarboxylic acid (11.1 g. 0.03 M; 76% yield) having the structure below, with 12% of 1 - hexadecylbenzene - 3 - methyl - 4 - carboxylic acid (1.62 g, 42 M moles; 10% yield).



(III)

x predominantly 5
y predominantly 7

The alkyl phthalic acid prepared as above was evaluated for its detergency building properties in the form of its sodium salt using the procedure and test conditions described for Example 1, with the following results.

Detergency builder	Soil removal (%) 12.5°H	25°H
Sodium 1-hexadecylbenzene-3,4-dicarboxylate	76	76
Sodium tripolyphosphate	79	71

This shows the alkyl phthalate system to be equivalent to the sodium tripolyphosphate

Detergency builder	% detergency for product concentration 0.2%	0.3%	0.4%
Disodium 3-pentadecyl phthalate	8	64	73
Sodium tripolyphosphate	46	70	76

Equivalence with the sodium tripolyphosphate is shown for the new detergency builder according to the invention at the higher product concentrations.

Example 4

Preparation of disodium 3-hydroxy-6-pentadecyl phthalate

Furfuryl bromide was prepared by dropwise addition of phosphorus tribromide (20 g) in dry ether to furfuryl alcohol 20 g in ether at 0°C. The reaction product was allowed to warm to ambient temperature and was then shaken with conc. sodium hydroxide solution (50 ml) and the ether layer was separated and dried. Dry, clean magnesium turnings (8 g) were suspended in ether with an iodine crystal as catalyst and then myristyl bromide was added in either at a rate maintaining reflux to form a solution of magnesium myristyl bromide. The solution of furfuryl bromide prepared as above was added with the Grignard reagent solution, again at a rate maintaining reflux, after which the mixture was cooled, poured onto ice and acidified with dilute sulphuric acid. The ethereal extract was washed, dried and then distilled under reduced pressure to give four fractions, one of which boiling at 130—150°C (at 0.8 mm Hg) was identified as pentadecyl furan. Dimethyl acetylene dicarboxylate (21.4 g) and pentadecyl furan (42 g) prepared as above were reacted at 100° for 8 hours and then cooled to 5—10°, diluted with 1,2 - dichloroethane and acidified with conc. sulphuric acid (6.4 g). The mixture was warmed to 20°, diluted with water, ether extracted and then worked up to give the 3 - hydroxy - 6 - pentadecyl phthalic acid, which was neutralised with sodium hydroxide solution at 20°C for 2 hours to give the disodium salt.

The disodium - 3 - hydroxy - 6 - pentadecyl phthalate was evaluated as a detergency builder using the procedure described in Example 1 with the following results:

system for fatty soil [redacted]val. The compound was also found to have appreciable fabric softening properties.

Example 3

Nonadec - 1 - ene - 3 - ol was prepared from hexadecyl magnesium bromide and acrolein in ether. The unsaturated alcohol (70 g) was heated with anhydrous potassium hydrogen sulphate (68 g) at 180° for 2 hours under reduced pressure, and the product was treated with water, extracted with ether and dried. Evaporation of the ether then gave a mixture of cis- and trans-nonadeca - 1,3 - diene. Equimolar proportions of maleic anhydride and the diene prepared as above were then heated under reflux in benzene for 6 hours after which the solvent was removed by distillation under reduced pressure. After washing the Diels-Alder reaction product with petroleum ether (40—60°), the product (11.5 g) was dehydrogenated with selenium dioxide (4.9 g) in boiling acetic anhydride for 6 hours. The precipitated selenium was removed by filtration and the filtrate was evaporated to give a red-brown product 3-pentadecyl phthalic anhydride, which was heated under reflux for 4 hours in a sodium hydroxide solution to yield the disodium salt.

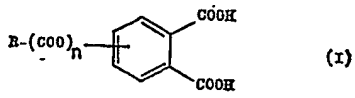
The disodium 3-pentadecyl phthalate prepared as described above was tested for detergency builder properties in the standard test described in Example 1 above (using 25°H water) with the following results at the product concentrations shown (with the same ratio of alkyl benzene sulphonate: builder).

% detergent 0.1% builder concentration
62.8

This result compares favourably with the result of 65.3% for sodium tripolyphosphate under comparable conditions.

WHAT WE CLAIM IS:—

1. A phthalic acid derivative which is a C_{10}—C_{20} alkyl or alkenyl substituted phthalic acid having the formula:



(I)

wherein R is an alkyl or alkenyl group containing from 10 to 20 carbon atoms, and n is 0 or 1, a hydroxyl group may be present in the benzene ring or the group R, or an alkali metal, ammonium or substituted ammonium salt or the anhydride thereof.

2. A compound according to claim 1 in the form of the disodium salt.

3. A compound according to claim 1 or claim 2, wherein n is 0.

4. A compound according to claim 1 or claim 2, wherein n is 1.

5. A compound according to claim 1 substantially as described herein with reference to any of the foregoing Examples.

6. A process for the preparation of an alkyl phthalic acid according to claim 3, by oxidation of an alkyl o-xylene in the presence of a bromide catalyst.

7. A process according to claim 6, wherein the catalyst is manganese bromide.

8. A process according to claim 7 substantially as described herein with reference to any of the foregoing Examples.

9. A process for the preparation of an alkyl phthalic acid according to claim 4, by reaction of a C_{10}—C_{20} acyl chloride with a hydroxy phthalic acid.

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